PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6:

(11) International Publication Number:

WO 99/18926

A61K 7/46, C11B 9/00, C11D 3/50

(43) International Publication Date:

22 April 1999 (22.04.99)

(21) International Application Number:

PCT/GB98/03057

A1

(22) International Filing Date:

9 October 1998 (09.10.98)

(30) Priority Data:

9721587.5

10 October 1997 (10.10.97) GB MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW,

ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF,

BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD,

GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN,

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR,

BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

INTERNATIONAL B.V. [NL/NL]; Huizerstraatweg 28, NL-1411 GP Naarden (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): PERRING, Keith, Douglas [GB/GB]; 14 Malvern Road, Ashford, Kent TN24 8HS (GB). CLEMENTS, Christopher, Francis [GB/GB]; Inveresk, Lookers Lane, Saltwood, Hythe, Kent CT21 5HW (GB). MACMASTER, Angus, Peter [GB/GB]; The Barn, Robus Ceramics, Evington Park, Hastingleigh, Nr Ashford, Kent TN25 5JH (GB).

(71) Applicant (for all designated States except US): QUEST

(74) Agents: HARRISON, David, C. et al.; Mewburn Ellis, York House, 23 Kingsway, London WC2B 6HP (GB).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PERFUME COMPOSITIONS

(57) Abstract

A perfume composition which gives good deposition and/or substantially improved deodorant effectiveness on textiles incorporating spandex® fibres. The perfume comprises a mixture of fragrance materials in which at least 60 % by weight of the composition comprises fragrance materials drawn from categories I and II.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
ΑU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	TE.	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL.	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of Americ
CA	Canada	rr	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NB	Niger	VN	Viet Nam
CG	Congo	KE	Кепуа	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
BE	Estonia	LR	Liberia	SG	Singapore		

10

15

20

PERFUME COMPOSITIONS

This invention relates to perfumes, to laundry compositions containing such perfumes, and the use of these compositions to deposit perfume on fabrics.

The use of perfumes in laundry products has been established for many years. Perfume is used to cover base odour and to provide fragrance notes which are attractive or pleasing to the consumer. Generally, it is important that a perfume be able to perform well olfactively at a number of stages, for example, from product 'in the pack', during product use, on damp cloth after laundering and on dry cloth (i.e. after drying the damp cloth). Certain perfumes have the ability to provide deodorant action against body odour, either when directly applied to human skin, or when included in a laundry product. Such perfumes are described in EP-B-3172, US-A-4304679, US-A-4278658, US-A-4134838, US-A-4288341 and US-A-4289641, US-A-5482635 and US-A-55554588.

It is important that sufficient fragrance should be transferred onto the fabric to be perceptible after laundering or (if the perfume has deodorant properties) to yield the deodorant effect.

10

15

20

25

A number of techniques have been proposed for increasing perfume delivery (to) and/or perfume longevity (on) substrates such as skin, hair, fabric and hard surfaces. This includes the use of fixative materials in the perfume to depress perfume ingredient partial pressures (eg GB 1534231) thereby reducing evaporative loss, and the use of carriers (eg EP 332259) or microcapsules (eg EP 376385) to deliver perfume to fabric. These technologies may increase perfume presence on dry cloth but involve further processing steps and/or material costs.

At the present time, many garments are made from fabric which contains a mixture of fibres, a proportion of which are elastic, so that the fabric has the ability to stretch and to recover from stretch. Spandex fibres are commonly used for this purpose. The term "spandex" has been adopted as a generic term by the United States Federal Trade Commission to denote a manufactured fibre in which the fibre-forming substance is a long chain synthetic polymer composed of at least 85% of a segmented polyurethane. A discussion of such fibres can be found in "History of Spandex Elastomeric Fibres" by A.J. Ultee, which is a chapter starting at page 278 in Man-Made Fibres: Their Origin and Development, edited by R.V. Seymour and R.S. Porter, Elsevier 1993. Spandex

fibres are also referred to as "elastane" or "elasthane" fibres.

Another discussion of such fibres is found under the heading "Segmented Polyurethanes" at page 613 of Handbook of Textile Fibres by J. Gordon Cook, 5th Ed. Merrow Publishing Company 1984. Further description of elastanes and their applications can be found in "Synthesefasern: Grundlagen, Technologie, Verarbeitung und Anwendung", B von Falkei (editor), 10 Verlag Chemie (1981). Commercially available elastanes are well known, in particular as sold under the name LYCRA®, a registered trade mark of DuPont de Nemours and Company. Patents relating to such fibres include US-A-5000899, US-A-5288779 and US-A-5362432.

15 Summary of the Invention

We have now discovered certain perfumes which give good deposition and/or substantially improved deodorant effectiveness on textiles incorporating spandex fibres.

Broadly, the present invention provides a perfume composition comprising a mixture of fragrance materials in which at least 60% by weight of the composition comprises fragrance materials drawn from the two categories below:

25 Category I

20

hydroxylic materials which are alcohols,

WO 99/18926

4

phenols or salicylates, with an octanol/water partition coefficient (P) whose common logarithm ($log_{10}P$) is 2.5 or greater, and a gas chromatographic Kovats index (as determined on polydimethylsiloxane as non-polar stationary phase) lying within the range 1050 to 1600.

PCT/GB98/03057

Category II

10

5

esters, ethers, ketones or aldehydes, with an octanol/water partition coefficient (P) whose common logarithm (log₁₀P) is 2.5 or greater, and a gas chromatographic Kovats index (as determined on polydimethylsiloxane as non-polar stationary phase) lying within the range 1300 to 1600.

15

20

Particularly preferred are category I materials with a partition coefficient whose common logarithm is 3.0 or greater and a Kovats index of 1100 up to 1600, and category II materials which are ethers, esters, or ketones with a Kovats index of 1350 up to 1600, and possessing one or more rings in their molecular structures.

It is envisaged that the perfumes of this invention will be incorporated into a laundry or other

composition for treatment of fabrics. This may be a detergent composition or presoak composition for washing the fabrics or a softening composition for softening the washed fabrics during rinsing and drying.

5

25

We have also discovered that the perfume may be incorporated into a composition used for treatment . of yarn or new fabric, to provide a perfume benefit on new garments.

De good deposition or retention of fragrance materials on the fabric. We have observed good deposition of a range of fragrance materials, especially fragrance materials which are of mid-range volatility (i.e. intermediate between the volatile perfume materials used as "top-notes" and the materials of low volatility which are customarily used as base notes in perfumes). These materials of mid-range volatility are often not perceptible on other fabrics such as cotton, polyamide and polyester after washing and drying.

Preferably, the perfume is a deodorant perfume giving a Malodour Reduction Value on cotton of at least 0.25, preferably at least 0.5, in the Malodour Reduction Value test described below and which is generally as given in EP-A-147191 and corresponding US-A-4663068.

With such perfumes we have observed that there is an enhanced deodorant benefit when the fabrics incorporate spandex fibres, compared to conventional fabrics such as cotton, polyamide and polyester without spandex. This can be measured using the Malodour Reduction Value test, modified by varying the test fabric instead of varying the perfume.

The Malodour Reduction Value Test

5

10

15

25

In this test, the Malodour Reduction Value of a deodorant perfume is measured by assessing its effectiveness, when applied to fabric, in reducing body malodour when the fabric so treated is placed in contact with the axillae (armpits) of a panel of human subjects, and held there for a standard period of time. From subsequent olfactory evaluation by trained assessors, a Malodour Reduction Value can be calculated so giving a measure of the effectiveness as a deodorant of the perfume under test.

Stage 1 is preparation of the perfume treated 20 fabric.

A fabric is selected for the test and cut into 20 cm x 20 cm squares. A control fabric is likewise cut into squares. Both fabrics are then washed in a front-loading drum-type washing machine with a standard unperfumed washing powder containing the following ingredients:

10

15

20

25

Ingredient	Parts by weight
Sodium dodecylbenzene sulphonate	9.0
C ₁₃₋₁₅ alcohol 7EO	4.0
Sodium tripolyphosphate	33.0
Alkaline sodium silicate	6.0
Sodium carboxymethyl cellulose	1.0
Magnesium silicate	1.0
Ethylenediamine tetraacetic acid	0.2
Sodium sulphate	15.0
Water	10.8

The washed pieces of fabric are then rinsed with cold water and finally dried. The fabric squares so obtained represent "untreated" fabric, that is fabric devoid of perfume, other deodorant materials, dressing and other water-soluble substances that subsequently might adversely affect the Malodour Reduction Value Test.

The untreated pieces of fabric are divided into two batches, one of which may receive no further washing treatment and then represents the control fabric in the test. The other batch of fabric pieces is re-washed in the washing machine with the same standard fabric washing powder to which has been added 0.2% by weight of the perfume under test. The perfume treated pieces of fabric are then rinsed with cold water and dried again. The fabric squares so obtained represent "test" fabric, that is fabric onto which the

test perfume has been delivered.

When the intention is to test perfume properties, the control and test fabrics are the same, e.g. polyester or cotton shirt fabric and the "untreated" fabric serves as control without further washing. To test deposition on different cloths, the test fabric can differ from the control fabric, and both may be washed with the perfumed washing powder.

team of three Caucasian female assessors of age within the range of 20 to 40 years is selected for olfactory evaluation on the basis that each is able to rank correctly the odour levels of the series of standard aqueous solutions of isovaleric acid listed below, and each is able to assign a numerical score, corresponding to the odour intensity of one of these solutions, to the body malodour of a shirt insert after has been worn in the axillary region by a male subject for a standard period of time.

A panel of 40 human subjects for use in the test is assembled from Caucasian male subjects of age within the range of from 20 to 55 years. By screening, subjects are chosen who develop axillary body malodour

WO 99/18926 PCT/GB98/03057

9

that is not unusually strong and who do not develop a stronger body malodour in one axilla compared with the other. Subjects who develop unusually strong body malodour, for example due to a diet including curry or garlic, are not selected for the panel.

5

10

15

For two weeks before the start of the test, the panel subjects are assigned an unperfumed, non-deodorant soap bar for exclusive use when washing and are denied the use of any other type of deodorant or antiperspirant. At the end of this period, the 40 subjects are randomly divided into two groups of 20.

The "test" and "control" fabric pieces are then tacked into 40 clean cotton or polyester-cotton shirts in the underarm region in such a manner that in 20 shirts, the control fabric pieces are attached inside the left underarm region, and the test fabric pieces are attached in the right underarm region. For the remaining 20 shirts, the placing of control and test pieces of fabric is reversed.

The shirts carrying the tacked-in fabric inserts are then worn by the 40 panel members for a period of 5 hours, during which time each panellist performs his normal work function without unnecessary

exercise.

5

10

15

After this five hour period, the shirts are removed and the inserts detached and placed in polyethylene pouches prior to assessment by the trained panel of assessors.

10

The malodour intensity of each fabric insert is evaluated by all three assessors who, operating without knowledge of which inserts are "test" and which are "control" and, without knowing the scores assigned by their fellow assessors, sniff each fabric piece and assign to it a score corresponding to the strength of the odour on a scale from 0 to 5, with 0 representing no odour and 5 representing very strong odour.

Standard aqueous solutions of isovaleric acid which correspond to each of the scores 1, 2, 3, 4 and 5 are provided for reference to assist the assessors in the malodour evaluation. These are shown below:

Score	Odour level	Concentration of aqueous isovaleric acid (ml/l)
0	No odour	0
1	Slight	0.013
2	Definite	0.053
3	Moderate	0.22
4	Strong	0.87
5	Very strong	3.57

20

The scores recorded by each assessor for each fabric piece are averaged. The average score of the "test" fabric pieces is deducted from the average score of the "untreated" control fabric pieces to give a Malodour Reduction Value.

As a check that the selection of panel subjects is satisfactory for operation of the test, the average score with untreated fabric pieces should be between 2.5 and 3.0.

have a Malodour Reduction Value of at least 0.50, or 0.70, or 1.00. The higher the minimum value, the more effective is the perfume as a deodorant as recorded by the assessors in the Malodour Reduction Value Test. It has also been noted that consumers, who are not trained assessors, can detect by self-assessment a noticeable reduction in malodour on soiled fabric such as shirts and underclothes where the Malodour Reduction Value is at least 0.30, so the higher the Malodour Reduction Value above this figure, the more noticeable is the deodorant effect.

Perfume Materials and Preferences

As mentioned above, the perfumes of this

invention must contain a number of fragrance materials specified by the presence of chemical structural groups, octanol/water partition coefficient(P) and Kovats index.

The octanol-water partition coefficient (or its common logarithm 'logP') is well known in the literature as an indicator of hydrophobicity and water solubility (see Hansch and Leo, Chemical Reviews, 526 to 616, (1971), 71; Hansch, Quinlan and Lawrence,

J.Organic Chemistry, 347 to 350 (1968), 33). Where such values are not available in the literature they may be measured directly, or approximately estimated using mathematical algorithms. Software providing such estimations are available commercially, for example 'LogP' from Advanced Chemistry Design Inc.

A requirement for $log_{10}P$ of 2.5 or more calls for materials which are somewhat hydrophobic.

Kovats indices are calculated from the retention time in a gas chromatographic measurement referenced to the retention time for alkanes [see Kovats , Helv.Chim.Acta 41, 1915 (1958)]. Indices based on the use of a non-polar stationary phase have been used in the perfumery industry for some years as

10

a descriptor relating to the molecular size and boiling point of ingredients. A review of Kovats indices in the perfume industry is given by T Shibamoto in "Capillary Gas Chromatography in Essential Oil Analysis", P Sandra and C Bicchi (editors), Huethig (1987), pages 259 to 274. A common non-polar phase which is suitable is 100% dimethyl polysiloxane, as supplied for example under a variety of tradenames such as HP-1 (Hewlett-Packard), CP Sil 5 CB (chrompack), OV-1 (Ohio Valley) and Rtx-1 (Restek).

The perfume materials fall into two sets referred to as categories I and II, differing in their minimum values of Kovats index.

formula ROH where the hydroxyl group may be primary,
secondary or tertiary, and the R group is an alkyl or
alkenyl group, optionally branched or substituted,
cyclic or acyclic, such that ROH has partition
coefficient and Kovats properties as defined above.

Typically this group comprises monofunctional alkyl or
arylalkyl alcohols with molecular weight falling
within the range 150 to 230.

Category I also includes phenols of general

10

15

20

formula ArOH, where the Ar group denotes a benzene ring which may be substituted with one or more alkyl or alkenyl groups, or with an ester grouping -CO₂A, where A is a hydrocarbon radical. As at the ortho position relative to the hydroxy group, the compound is a salicylate. ArOH has partition coefficient and Kovats index as defined above. Typically this group comprises monohydroxylic phenols with molecular weight falling within the range 150 to 210.

Ingredients which are particularly preferred are those with a partition coefficient of 1000 or more, i.e. log₁₀P of 3 or more, and a Kovats parameter of 1100 up to 1600.

Some examples of hydroxylic ingredients which fulfil the above criteria for category I are listed as a table below. Materials which are in the preferred sub-set are marked with an asterisk. Semitrivial names are those used in standard texts known within the perfume industry, particularly: Common Fragrance and Flavor Materials by Bauer, Garbe and Surburg, VCH Publ., 2nd edition (1990), and Perfume and Flavour Materials, Steffen Arctander, published in two volumes by the author (1969).

	· ·
	Examples of fragrance materials in category I
	1-(2'-tert-butylcyclohexyloxy)-butan-2-ol*
	3-methyl-5-(2',2',3'-trimethylcyclopent-3-enyl)-
	pentan-2-ol*
5	4-methyl-3-decen-5-ol*
	amyl salicylate*
	2-ethyl-4(2',2',3-trimethylcyclopent-3'-enyl)but-2-enol*
	(Bangalol, TM)
	borneol*
10	carvacrol*
	citronellol*
	9-decenol*
	dihydroeugenol*
	dihydrolinalol*
15	dihydromyrcenol
	dihydroterpineol *
	eugenol
	geraniol*
	hydroxycitronellal*
20	isoamyl salicylate*
	isobutyl salicylate*
	isoeugenol*
	linalol
	menthol*
25	nerolidol*
•	nerol*
	para tert-butyl cyclohexanol*
	phenoxanol*
	terpineol
30	tetrahydrogeraniol*
	tetrahydrolinalol
	tetrahydromyrcenol
	thymol*
	2-methoxy-4-methylphenol (Ultravanil, TM)
35	(4-isopropylcyclohexyl)-methanol*

Category II is esters, ketones , nitriles,

aldehydes or ethers which have an octanol-water partition coefficient whose common logarithm ($log_{10}P$) is at least 2.5, and a Kovats index of 1300 up to 1600 (non-polar phase).

formula RX, where X may be in a primary, secondary or tertiary position and is one of the following groups:

-COA, -OA, -CO₂A, -CN or -CHO. R and A are hydrocarbon residues, cyclic or non-cyclic and optionally

substituted. In some forms of this invention, category II excludes any material with a free hydroxy group, so that where a hydroxyl group is present, the material should be considered only for Category II membership.

Typically, the materials of Category II are

monofunctional compounds with molecular weights in the range 160 to 230.

Ingredients which are particularly preferred are those with a Kovats parameter falling within the range 1350 up to 1600, and possessing a molecular structure containing a ring, such as phenyl or cycloalkyl.

A number of fragrance materials which fulfil the above criteria for category II are listed in the

table below. Materials which are in the preferred subset are marked with an asterisk.

	Examples of fragrance materials in category II					
	1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-					
5	carbaldehyde*					
	1-(5',5'-dimethylcyclohexenyl)-pent-en-1-one*					
	2-heptyl cyclopentanone*					
	2-methyl-3-(4'-tert-butylphenyl)propanal					
	2-methylundecanal					
10	2-undecenal					
	2,2-dimethyl-3-(4'-ethylphenyl)-propanal					
	3-(4'-isopropylphenyl)-2-methylpropanal					
	4-methyl-4-phenylpent-2-yl acetate*					
•	allyl cyclohexyl propionate*					
15	allyl cyclohexyloxyacetate*					
	amyl benzoate*					
	methyl ethyl ketone trimers (Azarbre, TM)					
	benzophenone*					
	3-(4'-tert-butylphenyl)-propanal (Bourgeonal, TM)					
20	caryophyllene*					
	cis-jasmone*					
	citral diethyl acetal					
	citronellal diethyl acetal					
	citronellyl acetate					
25	phenylethyl butyl ether (Cressanther, TM)					
	damascone, alpha-*					
	damascone, beta-*					
	damascone, delta-*					
	decalactone, gamma-*					
30	dihydro isojasmonate*					
	dihydrojasmone*					
	dihydroterpinyl acetate					
	dimethyl anthranilate*					
	diphenyl oxide*					

	diphenylmethane*					
	dodecanal					
	dodecen-2-al					
	dodecane nitrile					
5						
J	3-(1'-ethoxyethoxy)-3,7-dimethylocta-1,6-diene					
	(Elintaal Forte (TM)					
	4-(4'-methylpent-3'-enyl)-cyclohex-3-enal (Empetaal,					
	TM)					
10	ethyl tricyclo[5.2.1.0~2,6~]decane-2-carboxylate*					
	1-(7-isopropyl-5-methylbicyclo[2.2.2]oct-5-en-2-yl)-1-					
	ethanone* (Felvinone, TM)					
	allyl tricyclodecenyl ether* (Fleuroxene, TM)					
	tricyclodecenyl propanoate* (Florocyclene, TM)					
15	gamma-undecalactone*					
	n-methyl-n-phenyl-2-methylbutanamide (Gardamide, TM)					
	tricyclodecenyl isobutyrate* (Gardocyclene, TM)					
	geranyl acetate					
	hexyl benzoate*					
20	ionone alpha*					
	ionone beta*					
	isobutyl cinnamate*					
	isobutyl quinoline*					
	isoeugenyl acetate*					
25	2,2,7,7-tetramethyltricycloundecan-5-one*					
:	(Isolongifolanone, TM)					
	tricyclodecenyl acetate* (Jasmacyclene, TM)					
	2-hexylcyclopentanone (Jasmatone, TM)					
-	4-acetoxy-3-pentyltetrahydropyran* (Jasmopyrane, TM)					
30	ethyl 2-hexylacetoacetate (Jessate, TM)					
	8-isopropyl-6-methylbicyclo[2.2.2]oct-5-ene-2- carbaldehyde (Maceal, TM)					
	methyl 4-isopropyl-1-methylbicyclo[2.2.2]oct-5-ene-2-					
	carboxylate*					
35	methyl cinnamate					
	alpha iso methyl ionone*					
	methyl naphthyl ketone*					
	nerolin					

30

	nonalactone gamma
	nopyl acetate*
	para tert-butyl cyclohexyl acetate
	4-isopropyl-1-methyl-2-[1'-propenyl]-benzene*
5	(Pelargene, TM)
	phenoxyethyl isobutyrate*
	phenylethyl isoamyl ether*
	phenylethyl isobutyrate*
	tricyclodecenyl pivalate* (Pivacyclene, TM)
10	phenylethyl pivalate* (Pivarose, TM)
	phenylacetaldehyde hexylene glycol acetal*
	2,4-dimethyl-4-phenyltetrahydrofuran (Rhubafuran, TM)
	rose acetone*
15	terpinyl acetate
	4-isopropyl-1-methyl-2-[1'-propenyl]-benzene
	(Verdoracine, TM)
	yara*
	(4-isopropylcyclohexadienyl)ethyl formate

Selection of a combination of fragrance

materials to give a deodorant effect is explained in

patents such as US-A-430679 referred to earlier.

Further systems of selection are given in US-A-5482635

and US-A-5554588 also mentioned above.

Such selections can be carried out using materials with preferred values of partition coefficient and Kovats index as discussed above.

The perfume compositions of this invention can deliver fragrance or, with appropriate perfume a deodorant benefit, to a range of fabrics, but the

10

benefit is particularly pronounced on fabrics containing spandex fibres.

The polymer which is spun into spandex fibres is a segmented polyurethane, that is a copolymer incorporating polyurethane linkages. The polymer generally contains so-called soft (i.e. lower melting) segments which may be polyalkylene ethers or polyesters and so-called hard (i.e. higher melting) segments which are portions derived from the reaction of an isocyanate and a chain extender which is typically a diamine.

The soft segments may be

poly(tetramethylene)ethers, possibly containing
substituted tetramethylene glycol residues as

15 described in US-A-5000899. Organic diisocyanates which
may be used include conventional diisocyanates, such
as diphenylmethane-4,4'-diisocyanate, also known as
methylene-bis (4-phenylisocyanate)or "MDI", 2,4tolylene diisocyanate, methylene-bis(4cyclohexylisocyanate), isophorone diisocyanate,
tetramethylene-p-xylylene diisocyanate, and the like.
MDI is preferred.

Chain extenders used in producing the hard

segment of the fibres preferably include one or more of ethylenediamine (EDA), 1,3-propylenediamine, 1,4-cyclohexanediamine, hydrogenated m-phenylenediamine (HPMD), 2-methylpentamethylene diamine (MPMD) and 1,2-propylene diamine. More preferably, the chain extender is one or more of ethylenediamine, 1,3-propylenediamine, and 1,4-cyclohexanediamine, optionally mixed with HPMD, MPMD and/or 1,2-propylenediamine.

5

15

20

poly(tetramethylene)ethers as the soft segments are marketed by Dupont de Nemours International S.A. under the registered trade mark LYCRA® of Dupont de Nemours and Company.

Spandex fibres are generally mixed with other fibres such as cotton, polyamide, wool, polyester and acrylics and made into yarn which is then made into fabric. The contents of spandex fibres is usually in a range from 0.5% by weight of the yarn or fabric up to 50%, more usually from 1% to 30% by weight of the yarn or fabric.

A wide range of garments may contain spandex fibres in the fabric, including active sports wear,

15

intimate apparel, hosiery and a variety of ready to wear casual clothing.

Fabric treatment compositions

Perfume compositions of the invention may be incorporated into fabric treatment products for use in washing, rinsing drying or other treatment of fabrics.

Such a product may be any of:

a detergent composition for fabric washing,

a pretreatment composition for application

to selected areas of a garment prior to

washing,

a pretreatment composition used in the soaking of entire garments prior to washing,

a rinse conditioner composition for softening washed fabrics during a rinsing step,

an additive composition for use jointly with any of the above,

a fabric conditioning article intended to be placed with fabrics during drying, or

a spray for application directly to dry garments.

5 Such products can take a variety of forms including powders, bars, sticks, tablets, mousses, gels, liquids, sprays, and also fabric conditioning sheets to be placed with fabrics in a tumble dryer. The amount of perfume in such products may lie in a 10 range from 0.1% to 10% by weight of thereof. The incorporation of perfume into products of these types is known, and existing techniques may be used for incorporating perfume for this invention. It may be possible to incorporate perfume directly into a 15 product, but another possibility is, to absorb the perfume on a carrier material and then admix the perfume-plus-carrier- mixture into the fabric treatment product. This approach may notably be used with a solid fabric treatment product and an inert 20 particulate carrier.

A detergent composition to be perfumed with a perfume composition according to this invention will

WO 99/18926 PCT/GB98/03057

normally contain a detersive surfactant in an amount from 2% to 50%, preferably 5 to 40% by weight of the composition, and a detergency builder in an amount from 5% to 80% by weight of the composition. The balance of the composition, if any, may include various ingredients known for inclusion in fabric washing detergents, including bleaching materials. Surfactants may be one or more soap or non-soap anionic, nonionic, cationic, amphoteric or zwitterionic surfactants, or combinations of these. Preferred surfactants which can be used are soaps and synthetic non-soap anionic and nonionic compounds. Mixtures of surfactants, for example mixed anionic or mixed anionic and nonionic compounds, are frequently used in detergent compositions.

Detergency builders are materials which function to soften hard water by solubilisation or other removal of calcium and to a lesser extent magnesium salts responsible for water hardness. The commonest water soluble inorganic builder is sodium tripolyphosphate. A further water soluble inorganic builder compound is sodium carbonate which is generally used in conjunction with a seed crystal to

WO 99/18926 PCT/GB98/03057

25

accelerate the precipitation of calcium carbonate.

Common insoluble inorganic detergency builders are

zeolites and layered silicates. Organic detergencybuilders such as sodium citrate and polyacrylate can
also be used.

5

Some detergent compositions, usually liquids, are formulated to contain from 5 to 50 wt% surfactant but little or no detergency builder.

included in a detergent composition, although not necessarily all together, include alkaline silicate, peroxygen or chlorine bleaches, soil release agents, heavy metal sequestrants, anti-redeposition agents such as sodium carboxymethyl cellulose, enzymes, enzyme stabilisers, fabric softening agents including softening clays, fluorescent brighteners, antifoam agents or conversely foam boosters and filler such as sodium sulphate.

Pretreatment compositions for soaking of

soiled fabrics prior to the main washing step may

contain 5 to 80 wt% by weight detergency builder with

little or no surfactant. Such compositions frequently

include enzymes.

20

The amount of perfume in a detergent composition or a presoak composition is likely to lie in a range from 0.1 to 2% by weight of the composition.

A fabric conditioning composition may contain from 1% to 40% by weight of a fabric conditioning agent which may be a fabric softening agent, but may contain higher levels in a very concentrated product.

Fabric softening agents are frequently nonionic or cationic organic compounds incorporating at least one alkyl, alkenyl or acyl group of 8 or more carbon atoms. These include, but are not limited to:

compounds and corresponding tertiary amines and imidazolines incorporating at least one, preferably two, C8 to C30 alkyl or alkenyl groups; also including alkyl groups containing, ether, ester, carbonate or amide linkages, ethoxylated derivatives and analogues of such compounds and also including compounds with more than one tertiary or quaternary nitrogen atom,

- (ii) aliphatic alcohols, esters, amines or carboxylic acids incorporating a C8 to C30 alkyl, alkenyl or acyl group, including esters of sorbitan and of polyhydric alcohols,
 - (iii) silicones, mineral oils and polyols such as polyethylene glycol.

A number of fabric conditioning compounds are set out in US-A-4137180, and EP-A-239910.

10 Fabric conditioning compositions for addition to a rinse liquid are frequently in the form of aqueous dispersions of the conditioning agent. They can also be made in the form of powders.

The amount of perfume in such conditioning
liquids and powders is usually 0.1% to 2% by weight.

Preferred levels can vary depending on the
concentration of softening agent and requirements of
the market.

The amount of perfume in very concentrated

fabric conditioners may lie in the broader range 0.1%

to 10% by weight, preferably 2% to 8% by weight.

10

15

20

A fabric conditioning sheet is intended to be placed with damp, rinsed, laundry in a tumble dryer.

Such a product contains a fabric conditioner, which may be a nonionic compound as mentioned above, soap and/or fatty acid, and which melts at temperatures encountered in a tumble dryer. This is carried on a porous sheet. Silicone oil may be included. The amount of perfume incorporated in such a product is usually from 2% to 10% of the product and frequently from 2% or 4% to 7% or 8% by weight of the product.

Another form of product for the treatment of fabrics is a carrier liquid containing perfume and packaged in an applicator which delivers the composition as a spray. Such a spray may be marketed as a "refreshing spray" for garments. In such a product, the content of perfume will generally lie in a range from 0.1% to 10% by weight of the liquid composition.

A further possibility is that the perfume is used in the treatment of yarn, or in the "finishing" of new fabric. This is a step in the wet processing of fabrics to improve hand or surface appearance of fabric. The fabric will typically be treated in an

aqueous treatment bath containing fabric softener to deposit at a level of up to 3% by weight of the fabric. Perfume according to this invention may be included in the bath to deposit at a level of 0.001% to 1% by weight of the fabric.

Example 1

10

15

20

A mixture of perfume ingredients was prepared and added to an unperfumed, but otherwise conventional, laundry detergent powder, to provide a perfume concentration of 0.5% by weight.

The perfumed powder was used to wash test cloths which had not previously been treated with any perfume. These were either all cotton, or 95% cotton with 5% spandex. After washing, the cloths were rinsed and then line dried overnight.

The perfume was extracted from the dry cloths with organic solvent, and the content of the perfume ingredients in the solvent extracts was determined by gas chromatography. If the concentration of an ingredient extracted from the spandex containing cloth was greater than from the all-cotton cloth by a factor of 5 to 20, the result was coded as a medium enhancement (M). If the concentration was greater by 20

or more, it was coded high(H) and if less than 5 or not measurable, it was coded(L).

The results obtained were as follows:

	<u> </u>				
	Ingredient	K*	logP**	Enhancement	Category
5	Boisambrene Forte	1714	5.5	М	-
	Benzyl acetone	1206	2.0	М	-
	Citronellol	1209	3.6	Н	I
	2,6-Dimethyl-heptan- 2-ol	975	2.9	L	-
10	Jasmacyclene	1394	2.9	Н	II
	Methyl salicylate	1167	2.3	L	-
	2-Phenylethanol	1087	1.4	L	-
	Terpinyl acetate	1331	4.0	Н	II
	Tetrahydrogeraniol	1180	3.6	Н	I
15	Tetrahydrolinalol	1083	3.5	H	I
	Tonalid .	1840	6.4	М	
	Yara	1416	3.2	Н	II

- * Measured on OV1 phase using capillary gc
- ** Measured or estimated using 'logP' software from ACD Inc.

Example 2

20

25

Two perfume compositions embodying this invention and a comparative composition contained perfume ingredients in the specified categories, as follows:

<u>Perfume</u>	Category I	Category II	<u>Other</u>
A	35.1	46.6	18.3
В	41.8	43.8	14.4
C	27.6	29.0	43.4

5 These were used in the procedure of the

Malodour Reduction Value test, as above, using test

cloths which were 95% cotton 5% spandex. For the

control, unperfumed washing powder was used to wash

all-cotton test cloths. The following results were

obtained:

	Perfume A	Perfume B	Perfume C
Average panel score:	1.04	1.29	1.57
Control panel score:	2.46	2.46	2.46
Malodour Reduction			
Value:	1.42	1.17	0.89
Malodour Reduction			
Value as % of control			
score:	57.7	47.4	36.1

<u>CLAIMS</u>

1. A perfume composition which is a mixture of fragrance materials characterized by containing at least 60 wt % of ingredients which are fragrance materials selected from:

Category I) hydroxylic materials which are alcohols, phenols or salicylates, with an octanol/water partition coefficient (P) whose common logarithm (log₁₀P) is 2.5 or greater, and a gas chromatographic Kovats index (as determined on polydimethylsiloxane as non-polar silicone stationary phase) lying within the range 1050 to 1600, and

Category II) esters, ethers, nitriles, ketones or aldehydes, with an octanol/water partition coefficient (P) whose common logarithm (log₁₀P) is 2.5 or greater, and a gas chromatographic Kovats index (as determined on polydimethylsiloxane as non-polar silicone stationary phase) lying within the range 1300 to 1600.

10

5

15

- 2. A perfume composition according to claim 1 containing at least 20 wt % of ingredients in said Category I.
- 3. A perfume composition according to claim 1
 5 containing at least 20 wt % of ingredients in said
 Category II.
 - 4. A perfume composition according to claim 1 containing at least 33 wt % of ingredients in said Category I.
- 10 5. A perfume composition according to claim 1 containing at least 30 wt % of ingredients in said Category II.
 - 6. A perfume composition according to any one of the preceding claims containing at least 20 wt % of ingredients in said Category I selected from the following list:

```
1-(2'-tert-butylcyclohexyloxy)-butan-2-ol
3-methyl-5-(2',2',3'-trimethylcyclopent-3-enyl)-

pentan-2-ol
4-methyl-3-decen-5-ol
amyl salicylate
2-ethyl-4(2',2',3-trimethylcyclopent-3'-enyl)-

but-2-enol (Bangalol, TM)
borneol

carvacrol
citronellol
```

	9-decenol	
	dihydroeugenol	
	dihydrolinalol	
	dihydromyrcenol	
5	dihydroterpineol	
	eugenol	
	geraniol	
	hydroxycitronellal	
	isoamyl salicylate	
10	isobutyl salicylate	
	isoeugenol	
	linalol	
	menthol	
	nerolidol	
15	nerol	
	para tert-butyl cyclohexanol	
	phenoxanol	
	terpineol	·
	tetrahydrogeraniol	
20	tetrahydrolinalol	
	tetrahydromyrcenol	
	thymol	·
	2-methoxy-4-methylphenol	(Ultravanil, TM)
	(4-isopropylcyclohexyl)-methan	nol

7. A perfume composition according to any one of the preceding claims containing at least 20 wt % of ingredients in said Category II selected from those in the following list:

```
1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-
carbaldehyde
1-(5',5'-dimethylcyclohexenyl)-pent-en-1-one
2-heptyl cyclopentanone
```

	2-methyl-3-(4'-tert-butylphenyl)propanal
	2-methylundecanal
	2-undecenal
	2,2-dimethyl-3-(4'-ethylphenyl)-propanal
5	3-(4'-isopropylphenyl)-2-methylpropanal
	4-methyl-4-phenylpent-2-yl acetate
	allyl cyclohexyl propionate
	allyl cyclohexyloxyacetate
	amyl benzoate
10	methyl ethyl ketone trimers (Azarbre, TM)
	benzophenone
	3-(4'-tert-butylphenyl)-propanal (Bourgeonal, TM)
	caryophyllene
	cis-jasmone
15	citral diethyl acetal
	citronellal diethyl acetal
	citronellyl acetate
	phenylethyl butyl ether (Cressanther, TM)
	damascone, alpha-
20	damascone, beta-
	damascone, delta-
	decalactone, gamma-
	dihydro isojasmonate
	dihydrojasmone
25	dihydroterpinyl acetate
	dimethyl anthranilate
	diphenyl oxide
	diphenylmethane
	dodecanal
30	dodecen-2-al
	dodecane nitrile
	1-ethoxy-1-phenoxyethane (Efetaal, TM)
	3-(1'-ethoxyethoxy)-3,7-dimethylocta-1,6-diene
	(Elintaal Forte (TM)
35	4-(4'-methylpent-3'-enyl)-cyclohex-3-enal
	(Empetaal, TM)
	ethyl tricyclo[5.2.1.0~2,6~]decane-2-carboxylate

	1-(7-isopropyl-5-methylbicyclo[2.2.2]oct-5-en-2-yl)- 1-ethanone (Felvinone, TM)
	allyl tricyclodecenyl ether (Fleuroxene, TM)
	tricyclodecenyl propanoate (Florocyclene, TM)
	gamma-undecalactone
	n-methyl-n-phenyl-2-methylbutanamide (Gardamide, TM)
	tricyclodecenyl isobutyrate (Gardocyclene, TM)
	geranyl acetate
	hexyl benzoate
	ionone alpha
	ionone beta
٠	isobutyl cinnamate
	isobutyl quinoline
	isoeugenyl acetate
	2,2,7,7-tetramethyltricycloundecan-5-one
	(Isolongifolanone, T
	tricyclodecenyl acetate (Jasmacyclene, TM)
	2-hexylcyclopentanone (Jasmatone, TM)
	4-acetoxy-3-pentyltetrahydropyran (Jasmopyrane, TM
	ethyl 2-hexylacetoacetate (Jessate, TM)
	8-isopropyl-6-methylbicyclo[2.2.2]oct-5-ene-2-carbaldehyde (Maceal, TM)
	methyl 4-isopropyl-1-methylbicyclo[2.2.2]oct-5-ene-2 carboxylate
	methyl cinnamate
	alpha iso methyl ionone
	methyl naphthyl ketone
	methyl naphthyl ketone nerolin
	nerolin
	nerolin nonalactone gamma
	nerolin nonalactone gamma nopyl acetate para tert-butyl cyclohexyl acetate 4-isopropyl-1-methyl-2-[1'-propenyl]-benzene
	nerolin nonalactone gamma nopyl acetate para tert-butyl cyclohexyl acetate
	nerolin nonalactone gamma nopyl acetate para tert-butyl cyclohexyl acetate 4-isopropyl-1-methyl-2-[1'-propenyl]-benzene (Pelargene, To
	nerolin nonalactone gamma nopyl acetate para tert-butyl cyclohexyl acetate 4-isopropyl-1-methyl-2-[1'-propenyl]-benzene (Pelargene, T

	phenylethyl pivalate (Pivarose, TM)					
	phenylacetaldehyde hexylene glycol acetal					
	2,4-dimethyl-4-phenyltetrahydrofuran (Rhubafuran, TM)					
5	rose acetone					
	terpinyl acetate					
	4-isopropyl-1-methyl-2-[1'-propenyl]-benzene					
	(Verdoracine, TM)					
	yara					
10	(4-isopropylcyclohexadienyl)ethyl formate					

- 8. A perfume composition according to any one of the preceding claims which is deodorant perfume having a malodour reduction value of from 0.5 to 3.0 as measured by the Malodour Reduction Test herein,

 15 carried out using 100% cotton fabric for both the test and the control pieces.
 - 9. Yarn or fabric containing spandex fibres, having a perfume composition according to any one of the preceding claims deposited on the said yarn or fabric.
 - 10. Use of a perfume composition as defined in any one of claims 1 to 8 in the treatment of yarn or fabrics containing spandex fibres.
- 11. A fabric treatment composition incorporating25 a perfume according to any one of the precedingclaims.

WO 99/18926 PCT/GB98/03057

38

12. A composition according to according to claim
11 which is a detergent composition for washing
fabrics, containing from 2 wt % to 50 wt % surfactant
and from 0.1 wt % to 5 wt % of the perfume
...
composition.

5

10

- 13. A composition according to claim 11 which is a rinse conditioner composition comprising an aqueous dispersion containing 1 wt % to 40 wt % of a fabric softening agent and from 0.1 wt % to 10 wt % of the perfume composition.
- 14. A method of treating yarn or unworn fabric comprising treating the yarn or fabric with a fabric finishing composition, characterised by incorporating a perfume according to any one of claims 1 to 8 into the finishing composition.

etional Application No PCT/GB 98/03057

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/46 C11E C11B9/00 C11D3/50 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) IPC 6 C11B C11D Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Category Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. US 5 500 138 A (D.R.BACON ET AL.) 1,8-11, 19 March 1996 14 see claims A 2-7,12, 13 WO 97 31097 A (PROCTER & GAMBLE) X 1,8-11, 28 August 1997 14 see claims; tables 1,2 see page "Perfume B" A 2-7,12, 13 see page 36 "perfume D" see page 40 "Perfume J" -/--X Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-"O" document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled in the art. "P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 4 February 1999 19/02/1999 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 Van Moer, A

I national Application No PCT/GB 98/03057

Relevant to claim No

1,8-11, 14
2-7,12, 13
1,8-11, 14
2-7,12, 13
1-8
1-8
1-8
1-14
1-14

Information on patent family members

national Application No PCT/GB 98/03057

Patent document cited in search report		Publication date	Patent family member(s)		Publication date	
US 4304679	Α	<u> </u>	IE	47904 B	25-07-1984	
			IN	149765 A	10-04-1982	
			JP	1667132 C	29-05-1992	
			JP	3021599 B	25-03-1991	
			JP	54107910 A	24-08-1979	
			NL	7900211 A	16-07-1979	
			SE	438688 B	29-04-1985	
			SE	7801713 A	13-07-1979	
			ZA	7900127 A	27-08-1980	
EP 147191	Α	03-07-1985	AU	575100 B	21-07-1988	
			AU	3688884 A	04-07-1985	
			BR	8406656 A	22-10-1985	
·			CA	1253084 A	25-04-1989	
			GB	2151669 A,B	24-07-1985	
			GR	82517 A	08-04-1985	
			JP	3057960 B	03-09-1991	
			JP	60155298 A	15-08-1985	
			JP	2706410 B	28-01-1998	
			JP	6122895 A	06-05-1994	
			PT	79733 B	24-11-1986	
			US	4663068 A	05-05-1987	

Information on patent family members

Is attional Application No
PCT/GB 98/03057

Patent document		Publication		Patent family	Dublication
cited in search repor	t	date		member(s)	Publication date
US 5500138	Α	19-03-1996	AU	3832195 A	15-05-1996
		20 00 1550	BR	9509410 A	03-11-1998
			CN	1169157 A	31-12-1997
			CZ	9701164 A	
			EP		12-11-1997
				0787176 A	06-08-1997
			JP	10507793 T	28-07-1998
			WO	9612785 A	02-05-1996
WO 9731097	Α	28-08-1997	US	5668094 A	16-09-1997
US 5554588	Α	10-09-1996	CA	2082281 A	09-05-1993
			DE	69221087 D	04-09-1997
			、 DE	69221087 T	13-11-1997
		•	EP	0545556 A	09-06-1993
			ES	2104850 T	16-10-1997
			JP	5255689 A	05-10-1993
			MX	9206423 A	01-05-1993
			ZA	9208578 A	06-05-1993
US 5482635	Α	09-01-1996	CA	2010222 A	10.12.1000
00 0402000	^	03-01-1330		2019222 A	19-12-1990
			DE DE	69008048 D	19-05-1994
				69008048 T	03-11-1994
			EP	0404470 A	27-12-1990
			ES	2055329 T	16-08-1994
			JP	2746735 B	06-05-1998
			JP	3054300 A	08-03-1991
			US	5501805 A	26-03-1996
			AU	6578394 A	21-11-1994
			BR	9406622 A	30-01-1996
			EP	0695166 A	07-02-1996
			WO	9424999 A	10-11-1994
			JP	2791610 B	27-08-1998
			JP	8509489 T	08-10-1996
			ZA	9402960 Å	30-10-1995
US 4604488	Α	05-08-1986	JP	1412208 C	27-11-1987
			JP	59116242 A	05-07-1984
			JP	62020173 B	05-07-1984
			CH	657868 A	30-09-1986
			. DE	3346213 A	
			FR		05-07-1984
			- г к	2539624 A	27-07-1984
US 4304679	Α	08-12-1981	AR	227130 A	30-09-1982
			AT	15879 A	15-05-1987
			AU	521125 B	18-03-1982
•			AU	4322479 A	19-07-1979
			BR	7900156 A	14-08-1979
			CA.	1122902 A	04-05-1982
			CA	1218018 B	17-02-1987
			DE	2900721 A	19-07-1979
			DE	2967667 A	12-11-1987
			DK	66078 A,B,	
			EP	000/0 H,B,	13-07-1979
				0003172 A	25-07-1979
			FI	780440 A	13-07-1979
			FR	2414551 A	10-08-1979
			GB	2012302 A,B	25-07-1979
			GR	66547 A	26-03-1981
		٠.	HK	42384 A	18-05-1984